

# The low temperature interface between the gas and solid phases of hard spheres with a short-ranged attraction

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## Abstract

At low temperature, spheres with a very short-ranged attraction exist as a near-close-packed solid coexisting with an almost infinitely dilute gas. We find that the ratio of the interfacial tension between these two phases to the thermal energy diverges as the range of the attraction tends to zero. The large tensions when the interparticle attractions are short-ranged may be why globular proteins only crystallise over a narrow range of conditions.

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## 1 Introduction

The interfacial tension is a useful quantity to know, it not only defines the cost of an interface but is also a central feature in the classical nucleation theory of first order phase transitions [1]. However, the interfacial tension between solid and fluid phases is unknown for all but a very few off-lattice microscopic models. Even for the very simple hard-sphere potential a consensus on its value has only recently been reached [2, 3]. This is despite the fact that we have known the bulk phase diagram of hard spheres for thirty years [4]. The reason for the lack of calculations of surface tensions is due to their difficulty: calculation of the interfacial tension of hard spheres is a formidable problem in density functional theory [2, 3]. Here we calculate the interfacial tension of hard spheres with a very short-ranged attraction. The limiting case when the range tends to zero is the  $\beta_0$  model of Stell [5, 6]. The phase behaviour of the  $\beta_0$  model is straightforward, if a little peculiar. Above a certain temperature  $T_{coll}$  the behaviour is identical to that of hard spheres (below close packing [7]) and below this temperature they phase separate into an infinitely dilute gas coexisting with a close-packed solid [5–9].

The bulk solid phase of spheres with a very short-ranged attraction can be described, due to its very high density, accurately and simply using a cell theory [10]. We will extend our previous cell theory treatment of the bulk [9] to the interface in order to calculate the interfacial tension analytically. Of course, the interfacial tension between a solid and another phase depends on the orientation of the interface with respect to the lattice of the solid. We calculate it when the surface of the solid is one of a few of the low index lattice planes.

The  $\beta_0$  limit with its zero ranged attraction is a purely mathematical limit, unobtainable in an experiment. However, there are two types of colloidal systems where the attraction has a range which is small in comparison to that of the hard repulsive interaction. These are mixtures of colloidal particles with either smaller particles [11–14] (which may be surfactant micelles [15]) or small polymer coils [16], and globular protein molecules [17–20].

## 2 Model and bulk phase behaviour

First, we define the well-known square-well potential. It is the spherically symmetric pair potential  $u(r)$  defined by

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma < r \leq \sigma(1 + \delta) \\ 0 & r > \sigma(1 + \delta) \end{cases}, \quad (1)$$

where  $\sigma$  is the hard-sphere diameter, and  $r$  is the separation between the centres of the spheres. Here we will always be considering short-ranged attractions,  $\delta \ll 1$ . The first person to consider very short-ranged attractions was Baxter [21] who considered a potential with zero range,  $\delta = 0$ , and with a well-depth  $\epsilon/T$  adjusted so that the second virial coefficient was of order unity. This model is often termed the sticky-sphere model. Within it the second virial coefficient is used as a temperature like variable. However, Stell [5] showed that the sticky-sphere model was pathological, its fluid phase was unstable at all non-zero densities. Therefore, we will not consider this model but instead will follow Stell when we take the limit  $\delta \rightarrow 0$ , thus obtaining his  $\beta_0$  model [5].

The bulk phase behaviour of the  $\beta_0$  model is described in Refs. [5–7, 9]. If the two limits  $\delta \rightarrow 0$  and  $T/\epsilon \rightarrow 0$  are taken such that  $T > T_{coll}$  then the equilibrium phase behaviour is identical to that of hard spheres. If  $T < T_{coll}$  then the behaviour is radically different: a close-packed solid coexists with a fluid phase of zero density. This close-packed solid may be either face-centred cubic or hexagonal close-packed; both have the same number of nearest neighbours and the same maximum density and so will have very similar free energies. Because of this we do not specify which one is actually formed. The temperature  $T_{coll}$  is [5, 6, 9]

$$\frac{T_{coll}}{\epsilon} = \frac{2}{\ln(1/\delta)}. \quad (2)$$

Note that we have used energy units for the temperature, i.e., units in which Boltzmann's constant equals unity.

## 3 Interfacial tension

Above  $T_{coll}$  the interface between the coexisting fluid and solid phases is identical to that of hard spheres; see Refs. [2, 3, 22] for work on the interface between solid and fluid phases of hard spheres. Below  $T_{coll}$  the gas-solid interface will be very different. It will be very narrow. The free energies per particle ( $/T$ ) in the coexisting solid and gas phases approach  $-\infty$  as the  $\beta_0$  limit is taken, while at intermediate densities, all densities which are non-zero and below close packing, the free energy is much higher [9]. Thus we expect the density will remain almost at its value in the bulk solid even in the outermost layer of the solid before dropping abruptly to zero. We will calculate the surface tension on the basis that only the outermost layer of the solid differs from the bulk. The solid layer beneath it, and the gas phase right up to the solid, are assumed to be identical to the bulk solid and gas phases, respectively.

The free energy of a bulk solid phase can be estimated using a cell theory [10]. A cell theory starts from the 1-particle partition function  $q_1$  of a particle trapped in a cell formed from its neighbouring particles fixed at the positions they occupy in a ideal lattice. The free energy per particle  $a_s$  is then obtained from

$$\frac{a_s}{T} = -\ln q_1, \quad (3)$$

where  $q_1$  is defined to be in units of  $\sigma^3$ , and a term which is the logarithm of the thermal volume of a sphere divided by  $\sigma^3$  is neglected. For a close-packed solid  $q_1$  is, see Ref. [9],

$$q_1 \simeq \delta^3 \exp(6\epsilon/T) \quad \rho > \frac{\rho_{cp}}{(1 + \delta/2)^3}. \quad (4)$$

$\rho_{cp} = \sqrt{2}\sigma^{-3}$  is the close-packed density of a close-packed solid of hard spheres. The restriction on the minimum density of the solid ensures that the sphere is close enough to all twelve of its neighbours to interact via the attraction. Inserting Eq. (4) into Eq. (3) yields

$$\frac{a_s}{T} = -3 \ln \delta - \frac{6\epsilon}{T} \quad \rho > \frac{\rho_{cp}}{(1 + \delta/2)^3}. \quad (5)$$

The first term in Eq. (5) is the logarithm of the volume available to the centre of a sphere and the second term is (half) its energy of interaction with its twelve neighbours. The volume available to the centre of a sphere is not precisely  $\delta^3$  but is  $c\delta^3$ , where  $c$  is a prefactor of order unity. We have neglected the  $\ln c$  term in Eq. (5) as it is of order unity whilst the other terms diverge in the  $\beta_0$  limit.

Equation (5) gives the free energy per sphere in the interior of the solid phase. The free energy per sphere in the outermost layer will be different. It will be given by an expression of the form of Eq. (3) but in which  $q_1$  is replaced by the partition function of a particle in the outermost layer,  $q_1^s$ . A particle in the outermost layer has fewer neighbours than in the bulk; recall that the coexisting gas is at very low density so there are almost no interactions between the outermost layer and the gas. How many fewer neighbours depends on which lattice plane forms the outermost layer. We denote the number of missing neighbours by  $z_m$ , it is equal to three for an interface in the 111 plane of a face-centred-cubic lattice. So, the energy of a particle in the outermost layer is  $(6 - z_m/2)\epsilon$ . All we now need is the available volume for a particle in the outermost layer. The particle can only explore a volume greater than  $\sim \delta^3$  at a cost of no longer being within  $\delta$  of all its remaining  $12 - z_m$  neighbours and so increasing the energy. It is easy to see that if the particle moves over a distance much larger than  $\delta$  in any one direction then it can only remain within  $\delta$  of two particles: its motion consists of rolling over the surfaces of a pair of adjacent spheres and so is restricted to a volume of order  $\delta^2\sigma$ . Thus, the entropy gain ( $\times T$ ) is  $-T \ln \delta$  but the energy cost is  $(10 - z_m)\epsilon$ . For the solid to be stable the temperature must be below  $T_{coll}$ , Eq. (2), and so  $-T \ln \delta < 2\epsilon$ . The entropy gain is then only greater than the energy cost when  $z_m > 8$ . Similar arguments apply for allowing a particle to move over a distance much larger than  $\delta$  in two or three directions. This is only favourable when  $z_m > 7$  and  $z_m > 6$ , respectively. For any flat outer layer  $z_m$  will be less than six, and the outermost particles will rattle inside a volume of order  $\delta^3$  as they do in the bulk. This is consistent with our assumption that only the outermost layer of the solid differs from the bulk. The particles in the layer below the outermost layer interact with twelve neighbours and so have the same free energy as in the bulk, apart from corrections of order  $T$ .

So, for  $q_1^s$  we have

$$q_1^s \simeq \delta^3 \exp [(6 - z_m/2)\epsilon/T] \quad \rho > \frac{\rho_{cp}}{(1 + \delta/2)^3}, \quad (6)$$

which gives a free energy difference per particle between the outermost layer and the interior of the solid of

$$\frac{a_i - a_s}{T} = \frac{z_m \epsilon}{2T} \quad \rho > \frac{\rho_{cp}}{(1 + \delta/2)^3}. \quad (7)$$

This difference can be converted into a surface tension by dividing by the area per sphere in the outermost layer. (In doing so we are implicitly fixing the surface of tension to be that which fixes the surface excess number of particles to be zero [23].) For example, for a 111 surface the area per sphere is  $\sqrt{3}/2\sigma^2$  and  $z_m = 3$ , so

$$\gamma_{111} = \sqrt{3}\epsilon\sigma^{-2} \simeq 1.73\epsilon\sigma^{-2} \quad T < T_{coll}. \quad (8)$$

Similarly, for the 110 and 100 surfaces of a face-centred-cubic lattice the areas per sphere are  $\sqrt{2}\sigma^2$  and  $\sigma^2$ , respectively and the  $z_m$ 's are 5 and 4. Thus,  $\gamma_{110} = (5/(2\sqrt{2}))\epsilon\sigma^{-2} \simeq 1.77\epsilon\sigma^{-2}$

and  $\gamma_{100} = 2\epsilon\sigma^{-2}$ . The 111 surface has the lowest surface tension because it has the lowest ratio of number of missing bonds per surface sphere to area per sphere. The surface tensions are all of order  $\epsilon\sigma^{-2}$ . In the  $\beta_0$  limit the ratio  $\epsilon/T$  is infinite, recall that we are below  $T_{coll}$ . Thus, the ratio of the surface tension (expressed using the sphere diameter as a unit of length) to the thermal energy is infinite. As the range of attraction becomes very small the interfacial tension becomes very large.

The assumptions which underlie the derivation of Eq. (8) should be valid whenever  $\epsilon/T \gg 1$ ,  $\delta \lesssim 0.1$  and the fluid phase is highly dilute. The first restriction ensures that the interface is only one layer thick, the second that Eqs. (4) and (6) are valid, and the third that the outer layer of solid does not interact to a significant degree with the fluid phase. Under these conditions, Eq. (8) is a good approximation for the interfacial tension and this tension is high.

An interfacial tension of order  $\epsilon\sigma^{-2}$  is not a surprise. It is what we would obtain if we just approximated the surface tension by the *energy* per unit area needed to pull a block of solid apart to create two new surfaces; see the book of Israelachvili [24] where he estimates interfacial tensions using just such an approximation. Note that Eq. (8) has no explicit dependence on the range of the attraction  $\delta$ , and so is a rough estimate of the low temperature interfacial tension even of the Lennard-Jones potential. Then  $\epsilon$  would be the well-depth of the Lennard-Jones potential.

We now compare our results with the earlier work of Marr and Gast [25, 26]. This work was conducted within the Percus-Yevick (PY) approximation for sticky spheres [21]. PY for the sticky-sphere model was shown by Stell [5, 6, 8] to yield qualitatively incorrect results; it predicts vapour-liquid equilibrium at a temperature of  $\epsilon/(\ln(1/\delta))$ . This is below  $T_{coll}$ , Eq. (2), and so in fact the fluid phase is unstable at all non-zero densities. Thus the results of Marr and Gast [25, 26] are for the interface between phases which do not exist.

## 4 Discussion and Consequences

We have calculated the low temperature interfacial tension of hard spheres with a very short-ranged attraction and found that its ratio to the thermal energy per unit area is very large. Low temperature means below  $T_{coll}$ , Eq. (2). In the limit that the range of the attraction tends to zero,  $\delta \rightarrow 0$ , the  $\beta_0$  limit [5], then this ratio diverges. In this limit above  $T_{coll}$  the attractive part of the interaction has a negligible effect: all the equilibrium properties, including the interfacial tension are identical to those of hard spheres. At  $T_{coll}$ , the coexisting fluid and solid densities change discontinuously to zero and close-packing ( $\rho_{cp}$ ), respectively [5, 6, 9], and the interfacial tension jumps to that given by Eq. (8). If the range  $\delta$  of the attraction is very small but finite then the discontinuity at  $T_{coll}$  becomes a narrow temperature range [27] over which the fluid and solid densities at coexistence rapidly decrease and increase, respectively. Below this temperature range the density of the fluid is very low and our Eq. (8) for the interfacial tension will be accurate.

When the range of the attraction is very small there is only a narrow temperature range [27] separating a high-temperature regime in which the spheres are almost hard spheres and a low-temperature regime where they are almost at the low-temperature limit. By almost at the low-temperature limit we mean that there is a very dilute gas coexisting with a solid with a density near close packing, and the interfacial tension between the two phases is then very high. This may explain the finding of George and Wilson [28] that there is only a narrow slot in effective temperature within which globular proteins can be made to crystallise [18–20]. (Other, not necessarily contradictory, explanations have been proposed by Poon [29], and by ten Wolde and Frenkel [30].) The narrow slot may correspond to the narrow temperature range where the coexisting densities and interfacial tension are changing rapidly. Above this temperature range the spheres are hard-sphere-like and so only crystallise at high density, above a volume fraction of 0.49 — the density at which a fluid of hard spheres coexists with the solid [4]. At

this density the dynamics of crystallisation may be slow [31, 32] due to a nearby glass transition. Below this temperature range the interfacial tension is very large. The free energy barrier to nucleation varies as the cube of the interfacial tension, within classical nucleation theory [1]. Thus, the rate of homogeneous nucleation varies as  $\exp(-\gamma^3)$  and so is extremely small when the interfacial tension is large. We conclude that spheres with a short-ranged attraction only crystallise easily from a dilute solution over a narrow temperature range around  $T_{coll}$ : above it the spheres crystallise only at high density; below it the interfacial tension is large and hence homogeneous nucleation is extremely slow.

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